Supporting Information

The Cause for the Tremendous Acceleration of the Chloride Substitution via Base Catalysis in the Chloro Pentaammine Cobalt(III) Ion

Basile F. E. Curchod and François P. Rotzinger

Transmission Coefficient (κ) and Rate Constant for the Transformation of the Conjugate Base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ into the Hexacoordinated Intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$. For reactions involving spin changes, the transmission coefficient κ might be smaller than 1 and, therefore, its value was computed. This allowed the estimation of the rate constant for the transformation of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ into the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$. The rate constant k(TST) can be calculated via the Eyring equation[54,55] (eq 3, k_B: Boltzman's constant, h: Planck's constant, $\Delta G^{\ddagger}$: free activation enthalpy, R: gas constant, and T: absolute temperature).

$$k(\mathrm{TST}) = \kappa \frac{k_B T}{h} e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad (3)$$

In the formalism of the transition state theory (eq 3), κ cannot be obtained on the basis of available computed data in a straightforward manner. The semi-classical theory for the estimation of electron transfer rates (eq 4),[56] however, allows the treatment of diabaticity (non-adiabaticity).

$$k(\mathrm{ET}) = K_A \nu_n \kappa_{el} e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad (4)$$

K_A is the constant for the aggregation of the reactants, which is equal to 1 for the present unimolecular reaction. ν_n is the nuclear frequency factor, which is not available from MECP computations, but which can be estimated as ~150 cm^{-1} (the Co−Cl stretching frequency in the transition state). κ_{el} is the electronic transmission coefficient (eq 5), ν_{el} (eq 6) the electronic frequency factor, and H_{ab} the electronic coupling matrix element.

$$\kappa_{el} = \frac{2\left(1 - e^{-\frac{\nu_{el}}{2\nu_n}}\right)}{2 - e^{-\frac{\nu_{el}}{2\nu_n}}} \qquad (5)$$

$$\nu_{el} = \frac{g H_{ab}^2}{\sqrt{\lambda}}, \; g = 1.75 \times 10^{13} \text{kJ}^{-\frac{3}{2}} \text{s}^{-1} \qquad (6)$$

λ, the reorganizational energy, is available from the data in Tables 1 and 2: it amounts to 74.0 kJ/mol (=98.4-24.4 kJ/mol) based on the conjugate base and to 95.0 kJ/mol (=70.6+24.4 kJ/mol) based on the intermediate. These two λ values should be equal. The deviation might arise from unequal curvatures of the PESs of conjugate base and intermediate, which might be due to the different spin states of these two species. Their different spin states are responsible for substantially different Co−Cl, Co−N(H_2), and Co−N(H_3) bond lengths (Figures S2 and S4). As it will be shown below, λ based on the conjugate base could be inaccurate because of the underestimated energy of the (excited) triplet state of *cis*-$Co(NH_3)_4(NH_2)Cl^+$. Alternatively, λ is available via the Marcus equation (eq 7),[57] which is applicable, if the PESs of reactant (*cis*-$Co(NH_3)_4(NH_2)Cl^+$) and product (*cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$) are similar.

$$\Delta G^{\ddagger} = \frac{(\lambda + \Delta G^{o})^2}{4\lambda} \qquad (7)$$

Taking the OPBE values of $\Delta E^{\ddagger}$ (=37.8 kJ/mol, Table 1) and ΔE (=24.4 kJ/mol, Table 1) for $\Delta G^{\ddagger}$ and ΔG^{o}, respectively, 96.2 kJ/mol is estimated for λ, which is equal to the above-estimated value of 95.0 kJ/mol based on the hexacoordinated intermediate. H_{ab}, computed via spin-orbit CI as described (Computational Details), is half of the singlet-triplet splitting energy. Due to hardware limitations, only a lower and an upper value is available for H_{ab} (20.3 and 55.4 cm^{-1}, respectively). The rate constant for the conversion of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ into the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$, k_+, was estimated on the basis of eq 4, whereby $\Delta G^{\ddagger}$ was approximated by $\Delta E^{\ddagger}$ (Table S42). k_+ or k(ET), respectively, depends weakly on ν_n in the range of 50-300 cm^{-1}, it is insensitive to λ (in the range of 74.0 – 96.2 kJ/mol), but it increases by a factor of ~6.5 with

increasing H_{ab}. Thus, the average value of 37.85 cm^{-1} was used for H_{ab}. κ (eq 3) was estimated as the ratio of k(ET)/k(TST) (eq 3 with κ = 1 and eq 4). For H_{ab} = 20.3, 37.85, and 55.4 cm^{-1}, κ amounts to 0.02, 0.06, and 0.11, respectively, 0.06 being the most likely value (Table S42). The rate constants k_+ and k_-, estimated via the most probable parameters ν_n = 150 cm^{-1}, H_{ab} = 37.85 cm^{-1}, λ = 84.5 (or 96.2) kJ/mol, are 8.7×10^4 (or 8.2×10^4) s^{-1} and 1.6×10^9 (or 1.5×10^9) s^{-1}, respectively (Table S42).

Table S1. Total Energies of all of the Investigated Species

compound	electronic state	geometry	E_{tot}, Hartrees	
			OPBE	MCQDPT2
(i) reactant:				
$Co(NH_3)_5Cl^{2+}$	singlet	Tables S2 and S29	-443.002896	-441.152970
(ii) conjugate bases:				
trans-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	singlet	Figure S1, Table S3	-442.513909	-440.671441
cis-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	singlet	Figure S2, Table S4	-442.510467	-440.667007
(iii) substitution via the D mechanism (singlet):				
cis-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ ‡}$ (transition state)	singlet	Figure 2a, Table S5	-442.490991	-440.650122
cis-eq-tbp-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (trigonal bipyramidal pentaccordinated intermediate)	singlet	Figure 2b, Table S6	-442.496733	-440.653403
trans-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ ‡}$ (transition state)	singlet	Figure S3, Table S7	-442.477874	-440.634284
trans-eq-tbp-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (trigonal bipyramidal pentacoordinated intermediate)	singlet	Table S8	-442.499832	-440.658443
(iv) substitution via the D mechanism (triplet):				
cis-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (hexacoordinated intermediate)	triplet	Figure S4, Table S9	-442.501187	-440.658228
cis-$Co(NH_3)_4(NH_2)Cl^{+\ ‡}$ (MECP)	singlet and triplet (their energies are equal by definition)	Figure 4, Table S10	-442.496066	-440.652813[a]

cis-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ ‡}$ (transition state for the conversion of the hexacoordinated intermediate into the square pyramidal pentacoordinated intermediate)	triplet	Figure S5, Table S11	-442.498675	-440.655877
cis-bas-sqp-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (square pyramidal pentacoordinated intermediate)	triplet	Table S12	-442.499227	-440.656592
(v) rearrangements:				
eq-tbp-$Co(NH_3)_4(NH_2)^{2+}$ (trigonal bipyramidal pentacoordinated intermediate)	singlet	Figure 11, Table S13	-427.341700	-425.644323
bas-sqp-$Co(NH_3)_4(NH_2)^{2+}$ (square pyramidal pentacoordinated intermediate)	triplet	Table S14	-427.343180	-425.641891
$Co(NH_3)_4(NH_2)^{2+\ ‡}$ (MECP for the transformation of the trigonal bipyramidal into the square pyramidal intermediate)	singlet and triplet (their energies are equal by definition)	Table S15	-427.337857	-425.641212[b]
$Co(NH_3)_4(NH_2)^{2+\ ‡}$ (first transition state along the Berry pseudo-rotation)	singlet	Figure S6, Table S16	-427.320208	-425.623907
ap-sqp-$Co(NH_3)_4(NH_2)^{2+}$ (intermediate along the Berry pseudo-rotation)	singlet	Table S17	-427.330975	-425.633816
ap-sqp-$Co(NH_3)_4(NH_2)^{2+\ ‡}$ (second transition state along the Berry pseudo-rotation)	singlet	Figure S7, Table S18	-427.329858	-425.632407
(vi) stereomobile substitution via the I_d mechanism and triplet states:				
cis-$Co(NH_3)_4(NH_2)Cl\cdot N_3$	singlet	Figure S8, Table S19	-606.782607	
ax-tbp-$Co(NH_3)_4(NH_2)\cdots Cl(N_3)^{‡}$ (transition state)	triplet	Figure 7a, Table S20	-606.761152	
cis-$Co(NH_3)_4(NH_2)N_3\cdot Cl$	singlet	Figure S9, Table S21	-606.793981	

cis-$Co(NH_3)_4(NH_2)Cl{\cdot}OH_2^+$	singlet	Table S22	-518.895440
ax-tbp- $Co(NH_3)_4(NH_2)\cdots Cl(OH_2)^{+\,\ddagger}$ (transition state)	triplet	Table S23	-518.872888

(vii) stereomobile substitution via the D mechanism and triplet states:

ax-tbp- $Co(NH_3)_4(NH_2)\cdots Cl(OH)^{\ddagger}$ (transition state)	triplet	Figure 7b, Table S24	-518.196469[c]

(viii) other intermediates with triplet or quintet states:

cis-$Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl^+$ (charge transfer intermediate)	triplet	Figure S10, Table S25	-442.443208
cis-$Co(NH_3)_4(NH_2)Cl^+$ (intermediate)	quintet	Figure S11, Table S26	-442.485224
trans-$Co(NH_3)_4(NH_2)Cl^+$ (intermediate)	triplet	Figure S12, Table S27	-442.496270
trans-$Co(NH_3)_4(NH_2)Cl^+$ (intermediate)	quintet	Figure S13, Table S28	-442.485907
$Co(NH_3)_5Cl^{2+}$ (intermediate)	triplet	Table S30	-442.968014
$Co(NH_3)_5^{3+}$ (intermediate)	singlet	Table S31	-427.784795

(ix) vertical transitions:

trans-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	triplet[d]	Figure S1, Table S3	-442.467998
trans-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	triplet[e]	Figure S1, Table S3	-442.456812
trans-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	quintet	Figure S1, Table S3	-442.435709
cis-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	triplet[d]	Figure S2, Table S4	-442.472993
cis-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	triplet[f]	Figure S2, Table S4	-442.400167
cis-$Co(NH_3)_4(NH_2)Cl^+$ (conjugate base)	quintet	Figure S2, Table S4	-442.431340
cis-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (hexacoordinated intermediate)	singlet	Figure S4, Table S9	-442.474312

cis-eq-tbp-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (trigonal bipyramidal pentacoordinated intermediate)	triplet	Figure 2b, Table S6	-442.483100

(x) reaction of chloro pentaammine complexes of Cr(III), Ru(III), and Rh(III) via the Basolo-Pearson mechanism:

cis-$Cr(NH_3)_4(NH_2)Cl^+$ (conjugate base)	quartet	Table S32	-383.827041
cis-$Cr(NH_3)_4(NH_2)\cdots Cl^{+\ \ddagger}$ (TS) (transition state)	quartet	Figure S14, Table S33	-383.810440
cis-eq-tbp-$Cr(NH_3)_4(NH_2)\cdot Cl^+$ (trigonal bipyramidal pentaccordinated intermediate)	quartet	Table S34	-383.814828
cis-$Ru(NH_3)_4(NH_2)Cl^+$ (conjugate base)	doublet	Table S35	-391.180824
cis-eq-tbp-$Ru(NH_3)_4(NH_2)\cdot Cl^+$ (trigonal bipyramidal pentaccordinated intermediate)	doublet	Table S36	-391.151687
cis-$Rh(NH_3)_4(NH_2)Cl^+$ (conjugate base)	singlet	Table S37	-407.350665
cis-eq-tbp-$Rh(NH_3)_4(NH_2)\cdot Cl^+$ (trigonal bipyramidal pentaccordinated intermediate)	singlet	Table S38	-407.321870

(xi) chloride substitution in chloro pentaammine chromium(III) by hydroxide via the I_a mechanism:

$Cr(NH_3)_5Cl\cdot OH^+$ (reactant)	quartet	Table S39	-460.217447
$Cr(NH_3)_5\cdots Cl(OH)^{+\ \ddagger}$ (TS) (transition state)	quartet	Figure 8, Table S40	-460.179524
$Cr(NH_3)_5OH\cdot Cl^+$ (product)	quartet	Table S41	-460.245486

[a]Average of singlet and triplet energies (which differ by 4.1 kJ/mol). [b]Average of singlet and triplet energies (which differ by 8.6 kJ/mol). [c]M06-L energy. [d]Lowest triplet state. [e]Higher triplet state, in which the σ^*(Co–Cl) MO is populated by one electron. [f]Charge transfer state representing *cis*-$Co^{II}(NH_3)_4(NH_2^\bullet)\cdots Cl^+$.

Table S2. Cobalt(III)–Ligand Bond Lengths[a] in the $Co(NH_3)_5Cl^{2+}$ Ion

compound	*d*(Co–Cl)	$d(Co–N)_{trans}$	$d(Co–N)_{cis}$	reference
$[Co(NH_3)_5Cl]SiF_6$	2.303±0.006	2.009±0.023	2.007±0.015[b] 1.974±0.015[b]	45
$[Co(NH_3)_5Cl]Cl_2$	2.286±0.002	1.964±0.006	1.962±0.004[b] 1.978±0.006 1.998±0.006	46
$Co(NH_3)_5Cl^{2+}$ (aq)[c]	2.260	1.970	1.963, 1.962, 1.963, 1.963	this work

[a]Units: Å. [b]Two symmetry equivalent bonds. [c]CPCM hydration.

Table S3. Atomic Coordinates (Å) of the Conjugate Base *trans*-$Co(NH_3)_4(NH_2)Cl^+$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2464731110	-0.0142268373	-0.0029949067
CL	17.0	2.1202234724	-0.0101512918	0.0052155984
N	7.0	-0.2497643445	1.9428397045	-0.0027397629
N	7.0	-2.1638795442	0.0773672406	-0.0053071404
N	7.0	-0.2621586621	0.0125009906	-1.9633705580
N	7.0	-0.2757170340	0.0166123223	1.9570641713
N	7.0	-0.2272031712	-1.9705831244	-0.0079673258
H	1.0	0.2017728898	2.3542679564	-0.8191034728
H	1.0	0.2039125550	2.3526169789	0.8132432965
H	1.0	-2.4727916438	-0.4724867634	-0.8171178546
H	1.0	-2.4749453325	-0.5086335142	0.7799268651
H	1.0	-1.1637110512	-2.3744589839	-0.0624405810
H	1.0	0.3092366117	-2.3371471632	-0.7945110932
H	1.0	0.2172710611	-2.3511477494	0.8276579734
H	1.0	0.6800767376	0.1906284053	-2.3136136580
H	1.0	0.6637540339	0.1945295687	2.3146792989
H	1.0	-0.8719152732	0.7445560914	-2.3290119983
H	1.0	-0.8878518126	0.7509580739	2.3140274463
H	1.0	-0.5771039278	-0.8593745020	-2.3897978892
H	1.0	-0.5960551110	-0.8526774234	2.3846413132
H	1.0	-1.2352967997	2.2139489462	-0.0011696019

Table S4. Atomic Coordinates (Å) of the Conjugate Base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2211382796	-0.0028390195	0.0021062760
CL	17.0	2.0646906031	0.0056177014	0.0016319347
N	7.0	-0.2114331109	2.0369201358	-0.0376911536
N	7.0	-2.1774499746	-0.0490618720	0.0081259145
N	7.0	-0.2353462940	-0.0434023404	-1.9586089377
N	7.0	-0.2371341682	-0.0211642749	1.9623811276
N	7.0	-0.3217107968	-1.9250955858	0.0390468742
H	1.0	0.5271751804	2.3644396264	-0.6596700297
H	1.0	-0.0064960812	2.4470812976	0.8730115217
H	1.0	-2.6169222019	0.3984054356	0.8126738647
H	1.0	-2.6234440335	0.3304639038	-0.8271830543
H	1.0	-2.3628012081	-1.0552583567	0.0505577556
H	1.0	0.1625478194	-2.2381061353	-0.8112097143
H	1.0	0.3541191902	-2.2041004418	0.7607596907
H	1.0	0.7168675707	-0.1691616692	-2.3036728642
H	1.0	0.7199945435	-0.0188008399	2.3167447352
H	1.0	-0.5940164692	0.8122031192	-2.3837544416
H	1.0	-0.7163851240	0.7720470313	2.3895617490
H	1.0	-0.7957552430	-0.8129020136	-2.3266507458
H	1.0	-0.6907064579	-0.8649017357	2.3146945943
H	1.0	-1.0818057674	2.4634694852	-0.3562665846

Table S5. Atomic Coordinates (Å) of the Transition State *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ ‡}$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.4475420025	-0.2537394397	0.1545014328
N	7.0	0.4969284336	1.4956120643	0.4640015085
N	7.0	-2.0991508202	0.6245988866	-0.2522774261
N	7.0	0.1932698468	-0.2114078117	-1.6836886089
N	7.0	-0.8644714762	-0.3604536834	2.0645553147
N	7.0	-0.8385615926	-2.0119722494	-0.0177827728
H	1.0	1.4930566725	1.2450278394	0.4984667882
H	1.0	0.2716088197	1.9703690476	1.3379208648
H	1.0	-2.3801349924	1.2971878787	0.4627963369
H	1.0	-2.0683649789	1.1299006546	-1.1389752582
H	1.0	-2.8442512199	-0.0701345846	-0.3283581901
H	1.0	-1.0789951241	-2.3675210292	-0.9460578171
H	1.0	-1.5220508570	-2.4259421808	0.6205897320
H	1.0	1.1898048253	-0.4467764019	-1.6163134135
H	1.0	-0.0343624575	-0.6758695580	2.5703419009
H	1.0	0.1263736024	0.6949069546	-2.1476841965
H	1.0	-1.1412973149	0.5256779157	2.4886906554
H	1.0	-0.2471306241	-0.8911837775	-2.3042828028
H	1.0	-1.6082467212	-1.0239715532	2.2845643038
H	1.0	0.3762137317	2.1895910574	-0.2737141567
CL	17.0	2.9053020315	-0.7094587298	0.3260460999

Table S6. Atomic Coordinates (Å) of the Trigonal Bipyramidal Pentacoordinated Intermediate *cis-eq-tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.7103306274	-0.3364625642	0.2342168266
N	7.0	0.6034671159	0.9935272986	0.8522453180
N	7.0	-1.8124871624	1.1721032834	-0.4617780825
N	7.0	0.2904929898	-0.4880652218	-1.4353488537
N	7.0	-1.6942784508	-0.2686325262	1.9290519751
N	7.0	-0.7383729560	-2.0875085560	0.3368780710
H	1.0	1.5479293234	0.6029398917	0.6758261239
H	1.0	0.5315416938	1.1799049419	1.8531558090
H	1.0	-2.0199000064	1.8970262455	0.2268197637
H	1.0	-1.4112261250	1.6561925965	-1.2660127940
H	1.0	-2.7134954341	0.8036556672	-0.7721464563
H	1.0	-0.2823881393	-2.7275841567	-0.3142682206
H	1.0	-1.1093053527	-2.6268645837	1.1201203995
H	1.0	1.2786968585	-0.6918142559	-1.2198889698
H	1.0	-1.1938922908	-0.7553286316	2.6745279957
H	1.0	0.2892050750	0.3646582083	-1.9957656037
H	1.0	-1.8698942376	0.6768108369	2.2711344306
H	1.0	-0.0618801157	-1.2300062762	-2.0409806778
H	1.0	-2.6072118735	-0.7184948014	1.8456702682
H	1.0	0.5611018062	1.8995522561	0.3833947450
CL	17.0	3.4322328811	-0.4603177093	-0.1228095383

Table S7. Atomic Coordinates (Å) of the Transition State *trans*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ ‡}$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.7882945726	-0.1998894080	-0.0762106520
N	7.0	0.3299374587	1.2986000987	0.2251861221
N	7.0	-2.5502851904	-0.7089373035	-1.1137740841
N	7.0	0.2345113892	-0.7422941486	-1.6501081073
N	7.0	-1.9042527536	0.3818562146	1.4089265343
N	7.0	0.2322765490	-1.2765588174	1.0053665889
H	1.0	0.8863560214	1.2206613258	1.0799686141
H	1.0	-0.2787240789	2.1449954658	0.3114677797
H	1.0	-3.2827421172	-0.0054773568	-1.0136495267
H	1.0	-2.4364129297	-0.8627342056	-2.1153563612
H	1.0	-2.9357152055	-1.5761049450	-0.7361136463
H	1.0	1.2156516074	-1.3068544133	0.7051437415
H	1.0	0.3019243507	-0.9156118094	1.9659394970
H	1.0	1.2468610724	-0.7275627695	-1.5158414870
H	1.0	-1.4210874448	0.3760865925	2.3085610076
H	1.0	0.0440828807	-0.1526994180	-2.4635505721
H	1.0	-2.2111612905	1.3552139405	1.2511436034
H	1.0	-0.0007143176	-1.6987294904	-1.9220989957
H	1.0	-2.7377955748	-0.1958514041	1.5277347258
H	1.0	0.9886003308	1.4618165562	-0.5385247160
CL	17.0	-1.8653000723	3.6393334222	0.5446725662

Table S8. Atomic Coordinates (Å) of the Trigonal Bipyramidal Pentacoordinated Intermediate *trans-eq-tbp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.5922067349	-0.2649708775	0.0209529799
N	7.0	0.2931943211	1.4899492242	-0.2295060060
N	7.0	-2.0500962979	0.4646468793	-1.1057690961
N	7.0	0.3192675400	-1.0223133735	-1.5413403871
N	7.0	-1.4865372074	0.4191506243	1.6136235020
N	7.0	-0.2563998498	-1.7519986205	0.8880258931
H	1.0	1.0952457251	1.5533829710	0.3994837876
H	1.0	-0.3356838921	2.2751813516	-0.0090540497
H	1.0	-2.3720402918	1.3849998631	-0.7725189063
H	1.0	-1.8061246962	0.5740808779	-2.0905250407
H	1.0	-2.8489428398	-0.1706103374	-1.0716195019
H	1.0	0.2441380809	-2.5592334638	0.5145003470
H	1.0	-0.5250733667	-1.9472510809	1.8529589470
H	1.0	1.2882654934	-1.2622201488	-1.3262095485
H	1.0	-0.8520036904	0.4576244411	2.4123979249
H	1.0	0.3518709623	-0.4036861265	-2.3524120531
H	1.0	-1.8550234145	1.3728643402	1.4687896383
H	1.0	-0.1344302449	-1.8815940086	-1.8554340234
H	1.0	-2.2729423919	-0.1716630111	1.8869018561
H	1.0	0.6483388772	1.6504983061	-1.1726319642
CL	17.0	-2.4228004840	3.4394341249	0.5089321668

Table S9. Atomic Coordinates (Å) of the Hexacoordinated Intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$ (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.3173254544	-0.0858512943	0.0053876480
CL	17.0	2.3859573110	0.1311270945	-0.0059630051
N	7.0	-0.1929530828	1.9449394639	-0.0313191185
N	7.0	-2.5240012796	0.1756005440	0.0164377364
N	7.0	-0.2506600686	-0.1119961905	-1.9754803260
N	7.0	-0.2522736711	-0.0883295911	1.9871173323
N	7.0	-0.2646493150	-1.8810854437	0.0125072567
H	1.0	0.7408002024	2.1813932728	-0.3684351526
H	1.0	-0.2941619862	2.3877641753	0.8810746408
H	1.0	-2.8679811558	0.8137917158	0.7325041537
H	1.0	-2.9075881484	0.4971435329	-0.8712022609
H	1.0	-2.9430225355	-0.7331021255	0.2045736642
H	1.0	0.0354593456	-2.3779245921	-0.8253278504
H	1.0	0.0936442160	-2.3711910681	0.8311968330
H	1.0	0.7251465552	-0.2029374574	-2.2609767893
H	1.0	0.7240605475	-0.0246669206	2.2785899842
H	1.0	-0.6135614118	0.7355085340	-2.4109420603
H	1.0	-0.7517287065	0.6893416495	2.4179723099
H	1.0	-0.7685780372	-0.8919082019	-2.3805166382
H	1.0	-0.6413492211	-0.9385923051	2.3947546383
H	1.0	-0.8726312640	2.3908775140	-0.6465734856

Table S10. Atomic Coordinates (Å) of the Minimum Energy Crossing Point *cis*-$Co(NH_3)_4(NH_2)Cl^{+\ ‡}$ for the Conversion of the Conjugate Base (*cis* Isomer) into the Hexacoordinated Intermediate

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.3498727362	-0.1660454167	0.0165058635
CL	17.0	1.8652591968	-1.3039886696	0.0161592113
N	7.0	0.6101846808	1.6400097320	-0.1452478037
N	7.0	-2.2200487037	0.9151727633	0.0120790565
N	7.0	-0.3844342423	-0.2906550931	-1.9691265280
N	7.0	-0.2617598935	-0.0451058164	2.0011879794
N	7.0	-1.2266950478	-1.7816057614	0.1430032496
H	1.0	1.5011847872	1.5246381950	-0.6261319951
H	1.0	0.8196306498	2.0734695223	0.7534575134
H	1.0	-2.3310887297	1.6398404210	0.7195193506
H	1.0	-2.4818828991	1.3259965821	-0.8828045098
H	1.0	-2.8984720231	0.1825806261	0.2147878360
H	1.0	-1.0287649733	-2.3796318422	-0.6632498509
H	1.0	-0.9051459660	-2.3199074071	0.9513901716
H	1.0	0.4918520637	-0.7076434768	-2.2851661687
H	1.0	0.6947551965	-0.2287869339	2.3056352742
H	1.0	-0.4708945642	0.6152562409	-2.4295777825
H	1.0	-0.5304687201	0.8689348307	2.3651496909
H	1.0	-1.1458871040	-0.8703422405	-2.3217460057
H	1.0	-0.8623484040	-0.7268949299	2.4643918617
H	1.0	0.0663910677	2.3237836372	-0.6716571610

Table S11. Atomic Coordinates (Å) of the Transition State *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ ‡}$ for the Conversion of the Hexacoordinated Intermediate into the Pentacoordinated one (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.4658810576	-0.2600242619	0.1785141200
N	7.0	0.5456195529	1.4390295024	0.5495991954
N	7.0	-2.3006292641	0.7403284408	-0.3369835548
N	7.0	0.2663011023	-0.2260324865	-1.6385793847
N	7.0	-0.9682066485	-0.3735664091	2.0807909253
N	7.0	-0.9224991525	-1.9796174855	-0.0386431400
H	1.0	1.5350900057	1.1512498691	0.5510815960
H	1.0	0.3512110597	1.8851027367	1.4454492587
H	1.0	-2.4112370814	1.6422779342	0.1253784379
H	1.0	-2.3843028022	0.9099867043	-1.3385069880
H	1.0	-3.1000076698	0.1683383784	-0.0691340042
H	1.0	-0.5844516447	-2.5303552437	-0.8260767306
H	1.0	-1.1003886136	-2.5937241505	0.7545449624
H	1.0	1.2650505614	-0.4510090916	-1.5531902774
H	1.0	-0.1782164848	-0.6487987363	2.6674985800
H	1.0	0.1905551897	0.6841515261	-2.0932258761
H	1.0	-1.3117245428	0.5147364206	2.4475035758
H	1.0	-0.1620965264	-0.9037352545	-2.2691703817
H	1.0	-1.7103575894	-1.0538911221	2.2477435001
H	1.0	0.4298875124	2.1559982135	-0.1662163475
CL	17.0	3.0347456096	-0.7180334805	0.2570280094

Table S12. Atomic Coordinates (Å) of the Square Pyramidal Pentaacoordinated Intermediate *cis-bas-sqp*-$Co(NH_3)_4(NH_2)\cdot Cl^+$ (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.5999398952	-0.3154349074	0.2698663832
N	7.0	0.6523160484	1.1746701404	0.7948257178
N	7.0	-2.1680885477	0.8875012087	-0.5499929968
N	7.0	0.4057388172	-0.4361270541	-1.4043934977
N	7.0	-1.4264280079	-0.2813613903	2.0558440146
N	7.0	-1.2191148337	-1.9820895348	0.0355976797
H	1.0	1.6224469984	0.8374353597	0.6712655677
H	1.0	0.5634895619	1.5036834612	1.7560735832
H	1.0	-2.4305878074	1.6708531803	0.0477311158
H	1.0	-1.9501056263	1.2776641665	-1.4662271123
H	1.0	-3.0007657523	0.3120937796	-0.6678436547
H	1.0	-0.8242498233	-2.6093788621	-0.6630113139
H	1.0	-1.5884195825	-2.5265334015	0.8136073707
H	1.0	1.4003035998	-0.6268644989	-1.1877889930
H	1.0	-0.8485818108	-0.7467090225	2.7587179978
H	1.0	0.3806777990	0.4389741221	-1.9292513832
H	1.0	-1.5916403594	0.6673400210	2.3942009957
H	1.0	0.0692356371	-1.1624128182	-2.0368614840
H	1.0	-2.3336013552	-0.7491046143	2.0628478457
H	1.0	0.5412839895	1.9932241792	0.1954494820
CL	17.0	3.4349268965	-0.5107895905	-0.0471311150

Table S13. Atomic Coordinates (Å) of the Trigonal Bipyramidal Pentacoordinated Intermediate *eq-tbp*-$Co(NH_3)_4(NH_2)^{2+}$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.6439963439	-0.2022240133	0.1464231646
N	7.0	0.0326038536	1.6542292577	0.3306379961
N	7.0	-2.4109756174	0.5859954945	-0.3039861659
N	7.0	-0.1095212671	-0.2259871769	-1.7355848630
N	7.0	-1.1418444287	-0.2688423884	2.0374893247
N	7.0	0.0305991752	-1.8086871786	0.3118590780
H	1.0	1.0539856840	1.6300321265	0.3412224117
H	1.0	-0.2528280581	2.1130468999	1.1968539343
H	1.0	-2.6940250923	1.3696628419	0.2863295870
H	1.0	-2.4802087489	0.9166198626	-1.2673892601
H	1.0	-3.1279381806	-0.1336980381	-0.1951655362
H	1.0	0.4789548821	-2.3441745335	-0.4325951994
H	1.0	0.0488303221	-2.3587213329	1.1715136997
H	1.0	0.8916734935	-0.4007143835	-1.8352685540
H	1.0	-0.3174945731	-0.3292898749	2.6376085916
H	1.0	-0.2972110734	0.6435068779	-2.2361918964
H	1.0	-1.6751403131	0.5399599504	2.3588901589
H	1.0	-0.5911661963	-0.9656172508	-2.2496583016
H	1.0	-1.7166879244	-1.0877229936	2.2421391799
H	1.0	-0.2353140268	2.2840681602	-0.4271240006

Table S14. Atomic Coordinates (Å) of the Square Pyramidal Pentacoordinated Intermediate *bas-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.5562998341	-0.1489251088	0.1730842271
N	7.0	0.0658634287	1.7752688467	0.3505226141
N	7.0	-2.5840706168	0.2303304051	-0.3671775796
N	7.0	0.0602489028	-0.1311655129	-1.6898731647
N	7.0	-0.9966884224	-0.1899808485	2.0842884936
N	7.0	-0.4757785087	-1.9377415277	0.1648304022
H	1.0	1.0387458058	1.8822336063	0.0565319898
H	1.0	0.0123768402	2.1545060298	1.2962244186
H	1.0	-2.8690375230	1.1963166822	-0.2044997182
H	1.0	-2.7695909861	0.0302343658	-1.3493284203
H	1.0	-3.2162703373	-0.3579900110	0.1740844068
H	1.0	-0.0003028658	-2.4456678809	-0.5795126011
H	1.0	-0.4381557757	-2.4758615744	1.0291528292
H	1.0	1.0734232713	-0.2451470077	-1.7632776972
H	1.0	-0.1635200579	-0.2401894373	2.6744712308
H	1.0	-0.1719617552	0.7388105516	-2.1712476545
H	1.0	-1.5181378154	0.6368862579	2.3794775849
H	1.0	-0.3605088491	-0.8841757762	-2.2358955923
H	1.0	-1.5772623098	-0.9941679831	2.3258029324
H	1.0	-0.4794604415	2.4043628420	-0.2406323069

Table S15. Atomic Coordinates (Å) of the Minimum Energy Crossing Point $Co(NH_3)_4(NH_2)^{2+}$ ‡ (Transformation of the Trigonal Bipyramid into the Square Pyramid)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.5824808944	-0.1759857446	0.1638636141
N	7.0	-0.0039574044	1.7640400481	0.3209405046
N	7.0	-2.5015451240	0.2985568375	-0.3364106896
N	7.0	0.0159488175	-0.1599377718	-1.7023006508
N	7.0	-1.0348502841	-0.2108255751	2.0707726731
N	7.0	-0.2223898873	-1.9094898572	0.2365768375
H	1.0	0.9847329065	1.8548554674	0.0793215063
H	1.0	-0.1010518454	2.1523286404	1.2596616579
H	1.0	-2.7606563477	1.2566291071	-0.0985287923
H	1.0	-2.6822631195	0.1801576362	-1.3334905001
H	1.0	-3.1519276333	-0.3142565352	0.1562325847
H	1.0	-0.0069974753	-2.4788431240	-0.5809471159
H	1.0	-0.4478805284	-2.5088514865	1.0294708754
H	1.0	1.0287325984	-0.2845258584	-1.7568666519
H	1.0	-0.1899677275	-0.2490322580	2.6444284644
H	1.0	-0.2000708971	0.7114813405	-2.1886417019
H	1.0	-1.5641263388	0.6082801051	2.3737235634
H	1.0	-0.4013990027	-0.9108426307	-2.2540115395
H	1.0	-1.5974533529	-1.0238909653	2.3251428562
H	1.0	-0.5067843100	2.3980895430	-0.3019111011

Table S16. Atomic Coordinates (Å) of the First Transition State $Co(NH_3)_4(NH_2)^{2+\ ‡}$ along the Berry Pseudo-Rotation (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.7336051198	-0.0648875911	0.1237102117
N	7.0	0.7387872039	1.0701708015	0.5176998675
N	7.0	-2.7630694186	0.0649787278	-0.4073153174
N	7.0	-0.2847396830	-0.0321210873	-1.7725869911
N	7.0	-1.2942098354	-0.0705285949	1.9914157582
N	7.0	0.2736270391	-1.5769474703	0.3785588402
H	1.0	1.6182293420	0.5577092523	0.6260554435
H	1.0	0.5957970931	1.5960642435	1.3822091867
H	1.0	-3.3069678891	0.6768554388	0.2017189852
H	1.0	-2.9381011453	0.3806497206	-1.3611512246
H	1.0	-3.1905943380	-0.8599373309	-0.3324490137
H	1.0	1.0897361008	-1.6218726552	-0.2456125155
H	1.0	0.6961475078	-1.6214761546	1.3151368389
H	1.0	0.7139310139	-0.1263995375	-1.9655956279
H	1.0	-0.5306801221	-0.2136316078	2.6547101546
H	1.0	-0.5853535985	0.8296477139	-2.2336092625
H	1.0	-1.7555249046	0.7992772592	2.2673257663
H	1.0	-0.7444886218	-0.8013233024	-2.2641105942
H	1.0	-1.9649228378	-0.8220914961	2.1636808540
H	1.0	0.8831588976	1.7579963826	-0.2248685458

Table S17. Atomic Coordinates (Å) of the Pentacoordinated Intermediate *ap-sqp*-$Co(NH_3)_4(NH_2)^{2+}$ Formed Along the Berry Pseudo-Rotation of the Trigonal Bipyramidal Intermediate (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.7485330990	0.0867061563	0.1208315983
N	7.0	0.9719342272	0.8716309331	0.5773342651
N	7.0	-2.5567393483	-0.5224236848	-0.3589574881
N	7.0	-0.2865230010	0.1646021631	-1.7722577221
N	7.0	-1.2985211456	0.1312659554	1.9928891505
N	7.0	-0.1531818524	-1.6829743952	0.2708826475
H	1.0	1.7148290494	0.1693624704	0.6150297755
H	1.0	0.9785035268	1.3423694949	1.4843484855
H	1.0	-3.3034046022	-0.1382493747	0.2232588007
H	1.0	-2.8278342988	-0.3396061669	-1.3264585072
H	1.0	-2.5550141676	-1.5362939282	-0.2331757481
H	1.0	0.6500442622	-1.7668244810	-0.3675892619
H	1.0	0.2953380302	-1.7514744966	1.1949329111
H	1.0	0.7173886190	0.1852452401	-1.9594460617
H	1.0	-0.5290735208	0.0392883549	2.6582294815
H	1.0	-0.6760252031	0.9983704167	-2.2216579990
H	1.0	-1.7736749028	1.0076622549	2.2274302745
H	1.0	-0.6512787274	-0.6389284238	-2.2868820877
H	1.0	-1.9512929538	-0.6216230502	2.2167999011
H	1.0	1.2734488338	1.5738149242	-0.1024886879

Table S18. Atomic Coordinates (Å) of the Second Transition State *ap-sqp*-$Co(NH_3)_4(NH_2)^{2+\ ‡}$ along the Berry Pseudo-Rotation (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.7546117071	0.0764685526	0.1261636842
N	7.0	0.9600976838	0.8965671027	0.5651059289
N	7.0	-2.5441483882	-0.5564937932	-0.3528824978
N	7.0	-0.3012903051	0.1921752717	-1.7800592294
N	7.0	-1.2577503166	0.1544240113	2.0054502527
N	7.0	-0.1194652674	-1.6863897757	0.2022553235
H	1.0	1.4286272457	0.4689969295	1.3661445043
H	1.0	0.8359322029	1.8846683822	0.8054395798
H	1.0	-3.1719988745	-0.7207403834	0.4353013654
H	1.0	-3.0377147869	0.0875091793	-0.9761994146
H	1.0	-2.4590382160	-1.4475525757	-0.8447267077
H	1.0	0.8782261167	-1.6201272238	0.4474315715
H	1.0	-0.5230715872	-2.0941676909	1.0570408875
H	1.0	0.5201488939	-0.3807888423	-1.9779456423
H	1.0	-0.4644969476	0.1441962308	2.6487355490
H	1.0	-0.0915971262	1.1423373651	-2.0963810819
H	1.0	-1.7698991995	1.0202514120	2.2012386571
H	1.0	-1.0389529681	-0.1591287695	-2.3917545115
H	1.0	-1.8672847394	-0.6079648466	2.3076419695
H	1.0	1.6382703069	0.8737625805	-0.1985354302

Table S19. Atomic Coordinates (Å) of the Conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl{\cdot}N_3$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	0.4828482400	0.1596773284	-0.8857582192
CL	17.0	2.5799240741	1.1122304390	-0.7860564344
N	7.0	1.2937977495	-1.5407725360	-1.4496402340
N	7.0	-0.3364872545	1.8564370908	-0.3777739072
N	7.0	-2.2888358258	0.6821016233	1.5757723558
N	7.0	-1.3022396466	-0.6201085137	-0.9625437243
N	7.0	0.5995985105	-0.3307828792	1.0859499378
N	7.0	0.1962130042	0.7081432838	-2.7120920809
H	1.0	0.5440737036	-0.0513007711	-3.3109377655
H	1.0	0.9127416260	1.4303928075	-2.8550103914
H	1.0	-0.2637367510	-0.0643272852	1.5725801392
H	1.0	0.7557792540	-1.3197552028	1.2783501985
H	1.0	1.3728072944	0.1755311998	1.5156280507
H	1.0	1.3116480184	-2.2535134961	-0.7194644837
H	1.0	2.2646130052	-1.3666433304	-1.7115430203
H	1.0	0.8366474763	-1.9664576431	-2.2567674835
H	1.0	-0.7487025994	2.2558828608	-1.2215082461
H	1.0	0.3573704490	2.5131790320	-0.0222907994
H	1.0	-1.0765241968	1.7347803816	0.3307933595
H	1.0	-1.8889076173	-0.2915993410	-0.1803194449
H	1.0	-1.6978130396	-0.2919939741	-1.8453459584
H	1.0	-1.3196260331	-1.6399706348	-0.9624584925
N	7.0	-3.2327047598	0.9898723563	2.2397948463
N	7.0	-4.1616288313	1.2889500375	2.9011086252

Table S20. Atomic Coordinates (Å) of the Transition State *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(N_3)^{‡}$ for the I_d Mechanism (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-1.6277831041	-0.4660268365	-0.5580276155
CL	17.0	1.7190854055	1.1122649585	1.2558561872
N	7.0	0.2196103668	-1.3074079849	-0.7877128419
N	7.0	-1.4142906610	1.5372757382	-0.2533979912
N	7.0	-3.8802910265	0.9499044038	1.5980010426
N	7.0	-3.3620220354	-1.4211987072	-0.1472878488
N	7.0	-1.2949735196	-0.6058323289	1.4260602667
N	7.0	-1.9421495721	-0.4795755850	-2.3487667472
H	1.0	-1.1803722162	-0.0599132926	-2.8897122225
H	1.0	-2.7941450716	0.0272826802	-2.6089844815
H	1.0	-2.0669453762	-0.1203508584	1.9032346649
H	1.0	-1.2584551304	-1.5643564723	1.7711569279
H	1.0	-0.4098116501	-0.1497510410	1.6770517984
H	1.0	0.2744341831	-2.2413952485	-0.3820541399
H	1.0	0.9134707258	-0.7200811572	-0.3084953707
H	1.0	0.4923264412	-1.3924099168	-1.7663672231
H	1.0	-1.4926738774	2.0886588813	-1.1061782892
H	1.0	-0.5102484028	1.7423648842	0.1871182660
H	1.0	-2.1697834298	1.8135887147	0.3847525527
H	1.0	-3.8792040219	-0.7784206354	0.4761093340
H	1.0	-3.9120561782	-1.5942365809	-0.9876825164
H	1.0	-3.2482030092	-2.3136948983	0.3317996118
N	7.0	-4.7105622249	1.4111439716	2.3239945805
N	7.0	-5.5293834299	1.8718273954	3.0356351752

Table S21. Atomic Coordinates (Å) of the Conjugate base *cis*-$Co(NH_3)_4(NH_2)N_3 \cdot Cl$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-1.9782555762	-0.1940538690	0.0458874132
CL	17.0	2.1172715664	0.7594994777	0.9449639251
N	7.0	-0.4370008697	-0.6859896404	-1.0727287259
N	7.0	-1.1627452838	1.5576952521	0.3624150156
N	7.0	-3.4762562940	0.2640135921	1.2161918827
N	7.0	-2.8060497725	-1.9440184024	-0.2976696018
N	7.0	-1.0106939639	-0.8961666346	1.6969317001
N	7.0	-2.7925926344	0.4701792621	-1.5646147135
H	1.0	-3.0612056574	1.4421984984	-1.3686422645
H	1.0	-3.7130991140	0.0169475488	-1.6218284323
H	1.0	-1.5069310541	-0.5768748695	2.5285764390
H	1.0	-0.9540432570	-1.9120010498	1.7634736158
H	1.0	-0.0498445362	-0.5474082852	1.7565853564
H	1.0	-0.3060474116	-1.6899606762	-1.1936080015
H	1.0	0.4520224867	-0.2992308874	-0.7394819938
H	1.0	-0.6683083595	-0.2839588550	-1.9833539279
H	1.0	-1.2246114834	2.1655829654	-0.4546432667
H	1.0	-0.1646835158	1.4844058465	0.6069193440
H	1.0	-1.6364266297	2.0341146744	1.1299843326
H	1.0	-3.7177549036	-1.9767075495	0.1595444091
H	1.0	-2.9579934028	-2.1060614707	-1.2938236949
H	1.0	-2.2724335720	-2.7412590528	0.0496257331
N	7.0	-4.3953294059	0.9816436893	0.9101451291
N	7.0	-5.3211284842	1.6633381763	0.7068065339

Table S22. Atomic Coordinates (Å) of the Conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl{\cdot}OH_2^+$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-1.0689395482	-0.2270158030	-0.0629489115
CL	17.0	1.0371569937	0.6976807091	-0.0477686104
N	7.0	-0.3100441650	-1.9312350983	-0.6551435494
N	7.0	-1.7796726406	1.5191096573	0.4674310013
O	8.0	-4.7536649917	0.9763726699	1.0101775357
N	7.0	-2.8461551446	-1.0423420840	-0.1027226882
N	7.0	-0.8550959755	-0.7442338039	1.8951238176
N	7.0	-1.3078124294	0.1562257409	-1.9329333475
H	1.0	-0.5612544168	0.8265270963	-2.1497001767
H	1.0	-2.1570903668	0.7313107856	-2.0047535442
H	1.0	-1.6276152349	-0.4316955818	2.4832611980
H	1.0	-0.7626603494	-1.7480503813	2.0491557870
H	1.0	-0.0064403058	-0.3149528832	2.2632713731
H	1.0	-0.7419155100	-2.7823648579	-0.2954228308
H	1.0	0.6905313968	-1.9829865504	-0.4658540074
H	1.0	-0.4463086149	-1.8984408814	-1.6680925565
H	1.0	-1.6712485982	2.1780320547	-0.3034048759
H	1.0	-1.2497696773	1.9007751912	1.2506791906
H	1.0	-2.7704361561	1.5139359184	0.7307944711
H	1.0	-3.5928876618	-0.4212127614	0.2436450791
H	1.0	-3.0606780600	-1.2825960182	-1.0713556993
H	1.0	-2.8980847787	-1.9042691188	0.4406123455
H	1.0	-5.4951425844	1.1461895481	0.4125660715
H	1.0	-5.1580868360	0.6385007852	1.8213684461

Table S23. Atomic Coordinates (Å) of the Transition State *ax-tbp*-$Co(NH_3)_4(NH_2)\cdots Cl(OH_2)^{+\ ‡}$ for the I_d Mechanism (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-1.5113588519	-0.4530718355	-0.5283037198
CL	17.0	1.8487639848	1.3283910869	1.3302117707
N	7.0	-0.1485065619	-1.8803679159	-1.0905910543
N	7.0	-1.0811947970	1.5055278265	-0.2064375368
O	8.0	-4.6268744264	1.0090488382	1.4454593914
N	7.0	-3.2865777100	-1.2162152596	0.1137838557
N	7.0	-0.8371815237	-0.7372962491	1.3576644097
N	7.0	-2.1358834480	-0.2930173729	-2.2214898354
H	1.0	-1.4474604967	0.0912354023	-2.8757978299
H	1.0	-2.9762127372	0.2884586795	-2.2896792293
H	1.0	-1.4684352162	-0.3334031339	2.0497595979
H	1.0	-0.7290745049	-1.7216998347	1.6008194954
H	1.0	0.0782816599	-0.2801566433	1.4890456865
H	1.0	-0.3979640516	-2.8025032488	-0.7325597475
H	1.0	0.8006558812	-1.6834650838	-0.7721923582
H	1.0	-0.1214705156	-1.9591230253	-2.1069614981
H	1.0	-1.1009921097	2.0468531324	-1.0699409451
H	1.0	-0.1450881737	1.6129251505	0.2250906951
H	1.0	-1.7627187793	1.9261754794	0.4263293482
H	1.0	-3.8258502631	-0.4854896141	0.6155915793
H	1.0	-3.8387990513	-1.5262279363	-0.6851024146
H	1.0	-3.1854797619	-2.0173999709	0.7358211996
H	1.0	-5.5345054487	1.0715518868	1.1148691539
H	1.0	-4.7294564688	0.8005200568	2.3850536665

Table S24. Atomic Coordinates (Å) of the Transition State *ax-tbp*-Co(NH_3)$_4$(NH_2)···Cl(OH)‡ for the stereomobile D Mechanism (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-1.5086011256	-0.4161950228	-0.5016658422
CL	17.0	1.5525975823	1.0608568151	0.9190015088
N	7.0	0.1926157838	-1.5478374501	-0.5834650630
N	7.0	-1.6784058798	1.5525787449	-0.0474900835
O	8.0	-3.5578799343	0.8402281538	1.6701310987
N	7.0	-3.4249321812	-1.1160343035	-0.1528121238
N	7.0	-1.3283078031	-0.5986179751	1.5156708864
N	7.0	-1.6928527457	-0.3730283458	-2.3450292066
H	1.0	-0.9219167501	0.1500343848	-2.7695001447
H	1.0	-2.5323371535	0.1502768947	-2.6047857042
H	1.0	-2.1684277044	-0.0702722559	1.8900930619
H	1.0	-1.3292968143	-1.5546746138	1.8618200615
H	1.0	-0.4553164361	-0.1549184060	1.8118198999
H	1.0	0.1354065048	-2.4357483081	-0.0907803468
H	1.0	0.9318804920	-0.9889916242	-0.1392039637
H	1.0	0.4724428661	-1.7512058836	-1.5400958888
H	1.0	-1.8870524068	2.1589400068	-0.8354018981
H	1.0	-0.7964411347	1.8616418339	0.3685614741
H	1.0	-2.4628662475	1.5679777977	0.6723710447
H	1.0	-3.7827391187	-0.4420899702	0.5759832283
H	1.0	-4.0233918004	-1.0991637964	-0.9741663869
H	1.0	-3.4673446251	-2.0593949277	0.2237943790
H	1.0	-4.0697122935	1.2198324563	2.3897402510

Table S25. Atomic Coordinates (Å) of the Intermediate *cis*-$Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl^{+}$ (Charge Transfer State, Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2616940162	0.1456666623	0.0036269732
CL	17.0	2.2563241416	-0.3515790815	0.0048815533
N	7.0	-0.4664553200	2.1371319134	-0.0369520600
N	7.0	-2.4553168955	-0.2384141324	0.0094628986
N	7.0	-0.2408056117	0.1169510366	-1.9790156135
N	7.0	-0.2392168575	0.1490792699	1.9858195056
N	7.0	0.0161916526	-1.9202891513	0.0135415243
H	1.0	0.2113881668	2.5716491927	-0.6642216842
H	1.0	-0.3338349362	2.5847719758	0.8701330770
H	1.0	-2.9619506620	0.1326877310	0.8122249153
H	1.0	-2.9570747005	0.0800438307	-0.8186568518
H	1.0	-2.5605373840	-1.2516045990	0.0410325589
H	1.0	0.4416709368	-2.3672759689	-0.8023089986
H	1.0	0.4377866553	-2.3667429183	0.8317820140
H	1.0	0.7195881252	0.1292639407	-2.3240027998
H	1.0	0.7060381745	0.3062194439	2.3368939732
H	1.0	-0.7265884182	0.8978174975	-2.4206782872
H	1.0	-0.8395532452	0.8536946525	2.4150531549
H	1.0	-0.6737543046	-0.7319040741	-2.3423544229
H	1.0	-0.5445978458	-0.7489407126	2.3603841428
H	1.0	-1.3898575370	2.4233533221	-0.3639502557

Table S26. Atomic Coordinates (Å) of the Intermediate *cis*-$Co(NH_3)_4(NH_2)Cl^+$ (Quintet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2125063639	-0.1033653681	0.0034332836
CL	17.0	2.2057288012	0.0279715470	0.0157828238
N	7.0	-0.2716185608	2.1082535107	-0.0452721801
N	7.0	-2.4133890050	0.0078134500	0.0036644627
N	7.0	-0.2214924897	0.0780861956	-2.1791680955
N	7.0	-0.2420254738	0.1125092179	2.1845162313
N	7.0	-0.2786685598	-1.9982468254	0.0035766067
H	1.0	0.4601818235	2.4489848829	-0.6658434936
H	1.0	-0.0890248623	2.5196749203	0.8679569692
H	1.0	-2.7724198472	0.6662269750	0.6929414523
H	1.0	-2.7922844894	0.2903459266	-0.8987635906
H	1.0	-2.8315322870	-0.8946808795	0.2238749940
H	1.0	-1.1076305720	-2.5906342194	-0.0024006637
H	1.0	0.5561433903	-2.5791419149	0.0568168405
H	1.0	0.7421139086	0.1226013523	-2.5052636267
H	1.0	0.6907465688	0.3567933040	2.5124883627
H	1.0	-0.7070911763	0.8884153550	-2.5601396274
H	1.0	-0.8861605085	0.8087806826	2.5557214891
H	1.0	-0.6417821934	-0.7483127586	-2.5988030814
H	1.0	-0.4855475946	-0.7761169892	2.6169872613
H	1.0	-1.1498635350	2.5043672983	-0.3763108452

Table S27. Atomic Coordinates (Å) of the Intermediate *trans*-$Co(NH_3)_4(NH_2)Cl^+$ (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2909797149	-0.0121222865	-0.0047945042
CL	17.0	2.0741144231	0.0181819683	0.0070435575
N	7.0	-0.1021780688	2.2484784527	-0.0242974412
N	7.0	-2.1019159431	0.0411289425	-0.0140077199
N	7.0	-0.3040665651	-0.0398742754	-1.9936001723
N	7.0	-0.3246849233	-0.0118026476	1.9841725799
N	7.0	-0.0931834230	-2.2388799443	0.0120930540
H	1.0	0.4521624891	2.5633437362	-0.8181946095
H	1.0	0.3747687954	2.5914580098	0.8074311588
H	1.0	-2.5688227589	0.4284135041	0.8059553799
H	1.0	-2.5616504794	0.3976253391	-0.8518314132
H	1.0	-1.0102461616	-2.6814047254	0.0130473160
H	1.0	0.4112737340	-2.5903816407	-0.7994414987
H	1.0	0.4071451368	-2.5782842872	0.8312985591
H	1.0	0.6397231270	-0.2168120665	-2.3366661170
H	1.0	0.6141722724	-0.1891595990	2.3402410176
H	1.0	-0.6133239504	0.8406564769	-2.4038158778
H	1.0	-0.6339782242	0.8753252330	2.3798116620
H	1.0	-0.9088485952	-0.7734308063	-2.3622586987
H	1.0	-0.9376605021	-0.7373207233	2.3551222369
H	1.0	-0.9992899997	2.7279525358	-0.0743278369

Table S28. Atomic Coordinates (Å) of the Intermediate *trans*-$Co(NH_3)_4(NH_2)Cl^+$ (Quintet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.3019794057	0.0053087687	-0.0053478298
CL	17.0	2.1550191542	-0.0075346264	0.0085400016
N	7.0	-0.0786528213	2.1767951783	-0.0247707542
N	7.0	-2.2076556349	0.0156838664	-0.0137421578
N	7.0	-0.3177114602	-0.0118304084	-2.1877773168
N	7.0	-0.3399554693	0.0185858032	2.1773034011
N	7.0	-0.1031480977	-2.1678979547	0.0113555048
H	1.0	0.4758401558	2.4900392399	-0.8190550914
H	1.0	0.3953698933	2.5152531206	0.8103064465
H	1.0	-2.8005115174	0.0202027589	0.8150360575
H	1.0	-2.7927070775	0.0222680698	-0.8480574908
H	1.0	-1.0090167178	-2.6326053482	0.0148288158
H	1.0	0.4081357828	-2.5053924608	-0.8018190767
H	1.0	0.4081812256	-2.4930137665	0.8295210423
H	1.0	0.6377922984	-0.0436576000	-2.5385457517
H	1.0	0.6121446602	0.0028123865	2.5382936642
H	1.0	-0.7550725278	0.8169869061	-2.5869056737
H	1.0	-0.7915596129	0.8470266953	2.5611012297
H	1.0	-0.8049886930	-0.8191813052	-2.5728646863
H	1.0	-0.8215004548	-0.7894591148	2.5681411781
H	1.0	-0.9781181249	2.6511147388	-0.0755036478

Table S29. Atomic Coordinates (Å) of the Reactant $Co(NH_3)_5Cl^{2+}$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2313904736	-0.0000317832	0.0020801019
CL	17.0	2.0287439780	-0.0115950483	0.0056044494
N	7.0	-0.1790919218	1.9621008959	-0.0353713356
N	7.0	-2.2009253356	-0.0098610392	0.0406089887
N	7.0	-0.2459730617	0.0046481313	-1.9601010668
N	7.0	-0.2438012394	0.0180489208	1.9649955100
N	7.0	-0.1824342441	-1.9621917193	-0.0273627275
H	1.0	0.5967128092	2.2650549976	-0.6258734488
H	1.0	-0.0070390292	2.3716508143	0.8835461000
H	1.0	-2.5912581402	0.8642885426	0.3960749736
H	1.0	-2.6171098090	-0.1570396748	-0.8803341448
H	1.0	-2.5685942074	-0.7468122431	0.6446001529
H	1.0	-1.0809269423	-2.4104847504	-0.2147828026
H	1.0	0.4666962964	-2.2810728031	-0.7476383364
H	1.0	0.1669637101	-2.3529829458	0.8482302100
H	1.0	0.7146020185	0.0325354470	-2.3065599654
H	1.0	0.7058296023	0.1650665284	2.3115110680
H	1.0	-0.7301544795	0.8112880461	-2.3570035502
H	1.0	-0.8283914521	0.7574619236	2.3575858696
H	1.0	-0.6844680190	-0.8238703021	-2.3651243219
H	1.0	-0.5785850940	-0.8529331100	2.3791056946
H	1.0	-1.0241541297	2.4048728192	-0.4000228248

Table S30. Atomic Coordinates (Å) of the Intermediate $Co(NH_3)_5Cl^{2+}$ (Triplet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2033272414	0.0030701732	0.0022590725
CL	17.0	2.1018435135	-0.0162298121	0.0092303834
N	7.0	-0.2504558694	2.1171946001	-0.0412878023
N	7.0	-2.3409832533	-0.0174889655	0.0473673069
N	7.0	-0.2252265861	0.0060388521	-1.9537818081
N	7.0	-0.2233559012	0.0218874245	1.9584382375
N	7.0	-0.2507408294	-2.1158676420	-0.0351876583
H	1.0	0.5055867972	2.4492010657	-0.6396060803
H	1.0	-0.0977180559	2.5380750410	0.8747685061
H	1.0	-2.7239776162	0.8579796590	0.4037562446
H	1.0	-2.7602377271	-0.1667436734	-0.8703307382
H	1.0	-2.6992440804	-0.7528026934	0.6566805110
H	1.0	-1.1703295548	-2.5131892894	-0.2276308563
H	1.0	0.3799829002	-2.4585723772	-0.7593067551
H	1.0	0.0736815733	-2.5269552461	0.8395576361
H	1.0	0.7320757241	0.0327995966	-2.3087085011
H	1.0	0.7228423728	0.1701729817	2.3131219175
H	1.0	-0.7171353984	0.8148995566	-2.3351634399
H	1.0	-0.8161731769	0.7626047820	2.3345039753
H	1.0	-0.6726543707	-0.8253216585	-2.3413385965
H	1.0	-0.5632349614	-0.8548558690	2.3546773821
H	1.0	-1.1164053620	2.5127857966	-0.4076098480

Table S31. Atomic Coordinates (Å) of the Pentacoordinated Intermediate $Co(NH_3)_5^{3+}$ (Singlet)

ATOM	CHARGE	X	Y	Z
CO	27.0	-0.2924786478	0.0018475544	0.0003504974
N	7.0	-0.1731591859	1.9471471836	-0.0413121791
N	7.0	-2.1684804007	-0.0063075272	0.0643625946
N	7.0	-0.1960862099	-0.0049825284	-1.9465835458
N	7.0	-0.1618623653	0.0140686503	1.9427400073
N	7.0	-0.1611024712	-1.9427326724	-0.0274580684
H	1.0	0.7547419650	2.2242002727	-0.3798891688
H	1.0	-0.2898856833	2.4028425485	0.8659546966
H	1.0	-2.5238436440	0.8240503274	0.5460006592
H	1.0	-2.5743494907	-0.0197628259	-0.8753360885
H	1.0	-2.5156557625	-0.8278834208	0.5666665491
H	1.0	-0.8306670655	-2.3932449836	-0.6553813811
H	1.0	0.7701806926	-2.2158637804	-0.3599182883
H	1.0	-0.2800853622	-2.3947551860	0.8813855840
H	1.0	0.7875913447	-0.0029213454	-2.2385376608
H	1.0	0.8258191275	0.0491434907	2.2188067157
H	1.0	-0.6246111267	0.8096939763	-2.3911674361
H	1.0	-0.6133836755	0.8148926130	2.3895551948
H	1.0	-0.6195679904	-0.8249997562	-2.3861283314
H	1.0	-0.5576300679	-0.8110472299	2.3977802713
H	1.0	-0.8487376699	2.3902612102	-0.6680494251

Table S32. Atomic Coordinates (Å) of the Conjugate Base *cis*-$Cr(NH_3)_4(NH_2)Cl^+$ (Quartet)

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.1251302747	-0.0350498329	0.0277669637
N	7.0	0.4306654092	2.0875393617	0.2571983252
N	7.0	-2.1339149734	0.6072550393	-0.2339828286
N	7.0	0.2215210704	0.1339870371	-2.0608609981
N	7.0	-0.4726645787	-0.1437555424	2.1242811685
N	7.0	-0.7699050414	-1.8823379441	-0.1386576602
H	1.0	1.4199259637	2.2111749428	0.0428110767
H	1.0	0.3021466562	2.4317636247	1.2084378128
H	1.0	-2.4166850277	1.3300990708	0.4278329501
H	1.0	-2.3337778844	0.9773655898	-1.1634982067
H	1.0	-2.7601003724	-0.1852980523	-0.0898175272
H	1.0	0.0393030178	-2.5046223074	-0.2198270530
H	1.0	-1.2812224392	-2.0138091817	-1.0171019456
H	1.0	1.0463248857	-0.4168634622	-2.2981839902
H	1.0	0.3910851258	-0.0819551289	2.6625739609
H	1.0	0.4069639771	1.0863229635	-2.3776701865
H	1.0	-1.1219488684	0.5379187400	2.5162578028
H	1.0	-0.5426997514	-0.2224823433	-2.6343345578
H	1.0	-0.8683474612	-1.0697833287	2.2857284195
H	1.0	-0.0810871493	2.7297229542	-0.3481056669
CL	17.0	2.1472182844	-0.6537685578	0.3572761771

Table S33. Atomic Coordinates (Å) of the Transition State *cis*-$Cr(NH_3)_4(NH_2)\cdots Cl^{+\ ‡}$ (Quartet)

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.4667339137	-0.0825327940	0.0259390524
N	7.0	0.5468651588	1.7966039163	0.3414069231
N	7.0	-2.2249222423	1.0230771266	-0.3192984533
N	7.0	0.1590276759	-0.0191011870	-1.9875891067
N	7.0	-0.8545712317	-0.2095856493	2.1052706029
N	7.0	-0.7281470705	-1.9246460258	-0.1109858768
H	1.0	1.5393174771	1.5410399163	0.4038003806
H	1.0	0.3047495214	2.2908970297	1.1999498600
H	1.0	-2.3976692200	1.7414466229	0.3845416858
H	1.0	-2.2253151101	1.4981720729	-1.2226882455
H	1.0	-3.0398836327	0.4076476330	-0.3157043304
H	1.0	-0.7551394648	-2.4356278329	-0.9918134279
H	1.0	-1.1524679503	-2.5013920181	0.6136081838
H	1.0	1.1541488494	-0.2554063649	-1.9904539562
H	1.0	-0.0388163219	-0.5748757637	2.5992862217
H	1.0	0.0694743597	0.8910017840	-2.4395968082
H	1.0	-1.0799565268	0.6831899439	2.5446999969
H	1.0	-0.3137675850	-0.6910289117	-2.5923281743
H	1.0	-1.6290329722	-0.8373673313	2.3234016257
H	1.0	0.4505574926	2.4736494379	-0.4152367155
CL	17.0	2.8436231777	-0.5119796100	0.2957387977

Table S34. Atomic Coordinates (Å) of the Trigonal Bipyramidal Pentacoordinated Intermediate *cis-eq-tbp*-$Cr(NH_3)_4(NH_2)\cdot Cl^+$ (Quartet)

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.7733737924	-0.1460914987	0.0545685673
N	7.0	0.7207988985	1.2630006295	0.5686853160
N	7.0	-2.1115749709	1.4602731980	-0.4236900049
N	7.0	0.0020558398	-0.1974370806	-1.9118538353
N	7.0	-1.5205246258	-0.1842904637	2.0349670458
N	7.0	-0.8649210904	-1.9883087368	0.0286900835
H	1.0	1.6598075343	0.8260414997	0.4648930418
H	1.0	0.6551941046	1.5965118725	1.5311778207
H	1.0	-2.1281167343	2.1980619995	0.2815215694
H	1.0	-1.8963338604	1.9219611322	-1.3082059382
H	1.0	-3.0735082814	1.1259313367	-0.5072023727
H	1.0	-0.5825451808	-2.5820385979	-0.7497937642
H	1.0	-1.1618259408	-2.5759610048	0.8065757402
H	1.0	0.9334680355	-0.6169119915	-1.9196508933
H	1.0	-0.8868713054	-0.6711457216	2.6709725504
H	1.0	0.1030368077	0.7237757204	-2.3393439981
H	1.0	-1.6717091808	0.7419506429	2.4360459420
H	1.0	-0.5734746117	-0.7489426888	-2.5496122957
H	1.0	-2.4164264919	-0.6704029261	2.0953218382
H	1.0	0.7193341711	2.0970499369	-0.0197793758
CL	17.0	3.6031150236	-0.2672469890	0.1230873093

Table S35. Atomic Coordinates (Å) of the Conjugate Base *cis*-$Ru(NH_3)_4(NH_2)Cl^+$ (Doublet)

ATOM	CHARGE	X	Y	Z
RU	44.0	-0.2478119947	-0.0284104986	0.0021093953
CL	17.0	2.1889658603	0.0086091266	0.0146960284
N	7.0	-0.1855735555	2.1754149804	-0.0290647196
N	7.0	-2.3843203245	-0.0588501318	-0.0061187613
N	7.0	-0.2085543059	-0.0048743198	-2.1430852588
N	7.0	-0.1862438004	0.0191969114	2.1448912479
N	7.0	-0.2486255267	-1.9625933864	0.0184356156
H	1.0	0.7562541234	2.4689295960	-0.2913754078
H	1.0	-0.3644592428	2.5949656736	0.8833570222
H	1.0	-2.8078015494	0.6098105463	0.6383253853
H	1.0	-2.7942561553	0.1367460985	-0.9202409179
H	1.0	-2.7384330631	-0.9761095106	0.2709231235
H	1.0	-1.0188780453	-2.5605026369	-0.2788759108
H	1.0	0.6017033141	-2.5019064273	0.1706251142
H	1.0	0.7470522697	0.1691839419	-2.4578706133
H	1.0	0.7564552229	0.2588428562	2.4552068079
H	1.0	-0.8039919872	0.6856360251	-2.6004899221
H	1.0	-0.8327667887	0.6545384947	2.6130956752
H	1.0	-0.4740686920	-0.9185121283	-2.5093558976
H	1.0	-0.3860480832	-0.9168387127	2.4964108153
H	1.0	-0.8301660849	2.6303860147	-0.6754278047

Table S36. Atomic Coordinates (Å) of the Trigonal Bipyramidal Pentacoordinated Intermediate *cis-eq-tbp*-$Ru(NH_3)_4(NH_2)\cdot Cl^+$ (Doublet)

ATOM	CHARGE	X	Y	Z
RU	44.0	-0.7681407022	-0.3689662226	0.2413045095
N	7.0	0.7927107335	0.7783469219	1.0796062280
N	7.0	-1.6784390187	1.4371392119	-0.5975277447
N	7.0	0.4087667988	-0.6518054708	-1.5203480182
N	7.0	-1.9636002600	-0.1890672745	2.0237133430
N	7.0	-0.7976227041	-2.2314032571	0.4572870750
H	1.0	1.7164100758	0.4529860157	0.7175911766
H	1.0	0.8179705964	0.7124686125	2.0984567832
H	1.0	-1.8671758921	2.1808518138	0.0764200545
H	1.0	-1.1507224785	1.8667324368	-1.3590736490
H	1.0	-2.5875726516	1.1908879805	-0.9956411224
H	1.0	-0.3132986848	-2.8974174026	-0.1470927615
H	1.0	-1.2612493120	-2.7220439963	1.2236963793
H	1.0	1.4159966758	-0.6244976075	-1.2985176100
H	1.0	-1.6456950915	-0.8105186529	2.7693827796
H	1.0	0.2523016058	0.0509791745	-2.2436429303
H	1.0	-1.9773825969	0.7467440575	2.4309875039
H	1.0	0.2285564179	-1.5511599674	-1.9697258185
H	1.0	-2.9414435699	-0.4310051883	1.8535272295
H	1.0	0.7199496447	1.7717513147	0.8529977830
CL	17.0	3.5428805949	-0.2813585076	-0.2491759998

Table S37. Atomic Coordinates (Å) of the Conjugate Base *cis*-$Rh(NH_3)_4(NH_2)Cl^+$ (Singlet)

ATOM	CHARGE	X	Y	Z
RH	45.0	-0.2342153569	0.0053254140	-0.0044926432
CL	17.0	2.1364696999	0.0097764987	-0.0024787116
N	7.0	-0.1806515151	2.1845791903	-0.0408485990
N	7.0	-2.3137033969	-0.0839251553	0.0257215535
N	7.0	-0.1765479923	-0.0474106975	-2.0873636206
N	7.0	-0.2212122615	-0.0860904841	2.0645414804
N	7.0	-0.3310509005	-2.0203859302	0.1537664947
H	1.0	0.7187005162	2.4839733298	-0.4170512908
H	1.0	-0.2514784720	2.5994679368	0.8877000641
H	1.0	-2.7463717616	0.5699402330	0.6784619810
H	1.0	-2.7561272956	0.0746815344	-0.8798347142
H	1.0	-2.5666378114	-1.0279286669	0.3252064663
H	1.0	-0.7196070905	-2.3830371829	-0.7254791105
H	1.0	0.6468152759	-2.3298706803	0.1133785214
H	1.0	0.7850650685	0.1254365750	-2.3846754334
H	1.0	0.7033724360	0.1338119686	2.4361985243
H	1.0	-0.7641855198	0.6390551224	-2.5609459615
H	1.0	-0.9021951028	0.4848228713	2.5648534353
H	1.0	-0.4336867976	-0.9652128241	-2.4533734266
H	1.0	-0.4161729176	-1.0710196079	2.2641715499
H	1.0	-0.9033687441	2.6273969913	-0.6076501614

Table S38. Atomic Coordinates (Å) of the Trigonal Bipyramidal Pentacoordinated Intermediate *cis-eq-tbp*-$Rh(NH_3)_4(NH_2)\cdot Cl^+$ (Singlet)

ATOM	CHARGE	X	Y	Z
RH	45.0	-0.7417426097	-0.3896417847	0.2543666003
N	7.0	0.7248675069	0.8985901295	1.0063161849
N	7.0	-1.5380540745	1.4305426427	-0.5268578032
N	7.0	0.4227417763	-0.7022489747	-1.4453551365
N	7.0	-1.9293222044	-0.1971623297	1.9788102409
N	7.0	-0.9875038947	-2.2470720331	0.3685323729
H	1.0	1.6527235712	0.5548902744	0.6812555520
H	1.0	0.7315684327	0.8695376333	2.0264165722
H	1.0	-1.6675528781	2.1835462052	0.1507624331
H	1.0	-0.9985962490	1.8276632008	-1.2975295177
H	1.0	-2.4633626638	1.2228131896	-0.9047016935
H	1.0	-0.5353985779	-2.9371763472	-0.2318790803
H	1.0	-1.4560775548	-2.7298425221	1.1354035240
H	1.0	1.4292982907	-0.6511554025	-1.2081677068
H	1.0	-1.5562237458	-0.7345225516	2.7625491204
H	1.0	0.2521669852	-0.0195457249	-2.1842653135
H	1.0	-2.0351364073	0.7612191854	2.3120400653
H	1.0	0.2548358413	-1.6163138905	-1.8671690046
H	1.0	-2.8742801378	-0.5438655984	1.8083822601
H	1.0	0.6611553428	1.8825174547	0.7401348108
CL	17.0	3.4939505792	-0.2407338471	-0.2602169441

Table S39. Atomic Coordinates (Å) of the Reactant $Cr(NH_3)_5Cl{\cdot}OH^+$ (Quartet)

ATOM	CHARGE	X	Y	Z
CR	24.0	-0.9899258712	0.0833067691	-0.0091473326
N	7.0	-2.1370559536	-0.9681171478	-1.4671263588
N	7.0	-2.0476500196	-0.9567503963	1.5211240503
N	7.0	0.4905867364	-1.3721111122	-0.0495113323
N	7.0	0.0967821876	1.0492792537	-1.5097320873
N	7.0	0.2526781997	1.0665354721	1.3493215942
H	1.0	-2.8406856539	-0.3454750381	-1.8652444089
H	1.0	-3.0469909929	-0.7616784259	1.4536741938
H	1.0	-2.6416257289	-1.7674567326	-1.0830742939
H	1.0	-1.9403309165	-1.9709829465	1.4870971964
H	1.0	-1.5873882460	-1.3272753841	-2.2479351086
H	1.0	-1.7667252318	-0.6690442020	2.4586348277
H	1.0	1.4186701323	-0.7756175843	-0.1217937681
H	1.0	0.4265039806	-2.0148772474	-0.8388725518
H	1.0	0.5224018689	-1.9462090739	0.7933095585
H	1.0	-0.1571761898	2.0345230217	-1.5751605816
H	1.0	0.0087536047	2.0525497138	1.4373936468
H	1.0	1.1200965922	0.9579953973	-1.2156665513
H	1.0	1.2367964068	0.9673169181	0.9295489214
H	1.0	-0.0225141940	0.6502625273	-2.4403985022
H	1.0	0.2522215833	0.6750893439	2.2909434882
CL	17.0	-2.6122245103	1.8099261344	0.0567035780
O	8.0	2.2820038348	0.4661070389	-0.1890862862
H	1.0	3.2445829006	0.4149904333	-0.1958360319

Table S40. Atomic Coordinates (Å) of the Transition State $Cr(NH_3)_5\cdots Cl(OH)^{+\ddagger}$ for the Cl^- Substitution by OH^- via the I_a Mechanism (Quartet)

ATOM	CHARGE	X	Y	Z
CR	24.0	0.0722904364	-0.0655049294	-0.0030603012
N	7.0	-1.3685293432	-0.3392101623	-1.5562644860
N	7.0	-1.3388975495	-0.3143239773	1.5788087744
N	7.0	0.2054128388	-2.1601929993	-0.0049664777
N	7.0	1.5031103095	0.0416665163	-1.5128727012
N	7.0	1.5257652035	0.0290403450	1.4875806104
H	1.0	-1.5390049649	0.5581367029	-2.0112720822
H	1.0	-1.3942677504	0.5476460139	2.1216560538
H	1.0	-2.2747616966	-0.6530808457	-1.2087569106
H	1.0	-2.2845743642	-0.4871206802	1.2383771515
H	1.0	-1.0880734520	-1.0050671745	-2.2766935699
H	1.0	-1.1172951436	-1.0710777392	2.2265989306
H	1.0	0.6907237107	-2.5048905658	-0.8338250895
H	1.0	-0.7078782531	-2.6160447851	0.0112732856
H	1.0	0.7218708960	-2.5073372782	0.8037859574
H	1.0	1.1771143633	0.0212867613	-2.4772092799
H	1.0	1.2140735607	-0.0126554398	2.4559599484
H	1.0	1.7653084789	1.0345484248	-1.1906707551
H	1.0	1.7786193542	1.0268155711	1.1791739824
H	1.0	2.3007244989	-0.5873292661	-1.4329414980
H	1.0	2.3263675544	-0.5925853323	1.3835255232
CL	17.0	-1.4958538494	2.3519639457	-0.0047546598
O	8.0	1.6408530612	2.0747034076	-0.0052224129
H	1.0	0.8375501270	2.6175734352	-0.0058375336

Table S41. Atomic Coordinates (Å) of the Product $Cr(NH_3)_5OH \cdot Cl^+$ (Quartet)

ATOM	CHARGE	X	Y	Z
CR	24.0	0.3999755539	-0.3506412752	0.0138510487
N	7.0	-1.0898309120	-0.0282366681	-1.4457860422
N	7.0	-1.0900184663	-0.0227317479	1.4712265279
N	7.0	0.0281740034	-2.4930975601	0.0171751045
N	7.0	1.8555733778	-0.6887093936	-1.5020121448
N	7.0	1.8446882889	-0.6722108075	1.5437900518
H	1.0	-1.6137537993	0.8257002495	-1.2055415989
H	1.0	-1.6063201852	0.8375652537	1.2352171692
H	1.0	-1.7726367292	-0.7817267416	-1.5319147073
H	1.0	-1.7797771627	-0.7706054645	1.5506589581
H	1.0	-0.7003911939	0.1198907412	-2.3770090698
H	1.0	-0.7011170128	0.1148595873	2.4042512674
H	1.0	-0.4696391976	-2.8191801817	-0.8119244959
H	1.0	-0.5205441583	-2.8099405195	0.8171862785
H	1.0	0.8968458325	-3.0277478109	0.0473536045
H	1.0	1.4903154271	-1.1489212384	-2.3361323504
H	1.0	1.5030900150	-1.2115011064	2.3397395014
H	1.0	2.2061055834	0.2243007904	-1.7939674061
H	1.0	2.1182529262	0.2452307433	1.8974291525
H	1.0	2.6659629808	-1.2353160174	-1.2101428037
H	1.0	2.7014134170	-1.1325642320	1.2358422305
CL	17.0	-2.3795279149	2.7845381978	0.0260142121
O	8.0	0.8659380654	1.4754947782	0.0064237542
H	1.0	0.0600375759	2.0234749346	0.0097613004

Table S42. Computation of the Rate Constants k_+ and k_-

	ν_n, cm^{-1}	H_{ab}, cm^{-1}	λ, kJ/mol	ν_{el}, s^{-1}	κ_{el}	$\Delta E^{\ddagger}$, kJ/mol	k(ET), s^{-1} (eq 4)	k(TST), s^{-1} (eq 3)	κ= k(ET)/k(TST)
k_+:	50	37.85	84.5	3.90E+11	0.22	37.8	7.78E+04	1.48E+06	0.05
	100	37.85	84.5	3.90E+11	0.12	37.8	8.48E+04	1.48E+06	0.06
	150	37.85	84.5	3.90E+11	0.08	37.8	8.75E+04	1.48E+06	0.06
	200	37.85	84.5	3.90E+11	0.06	37.8	8.88E+04	1.48E+06	0.06
	300	37.85	84.5	3.90E+11	0.04	37.8	9.02E+04	1.48E+06	0.06
	50	20.28	84.5	1.12E+11	0.07	37.8	2.53E+04	1.48E+06	0.02
	100	20.28	84.5	1.12E+11	0.04	37.8	2.60E+04	1.48E+06	0.02
	150	20.28	84.5	1.12E+11	0.02	37.8	2.62E+04	1.48E+06	0.02
	200	20.28	84.5	1.12E+11	0.02	37.8	2.64E+04	1.48E+06	0.02
	300	20.28	84.5	1.12E+11	0.01	37.8	2.65E+04	1.48E+06	0.02
	50	55.43	84.5	8.37E+11	0.39	37.8	1.40E+05	1.48E+06	0.09
	100	55.43	84.5	8.37E+11	0.23	37.8	1.65E+05	1.48E+06	0.11
	150	55.43	84.5	8.37E+11	0.16	37.8	1.75E+05	1.48E+06	0.12
	200	55.43	84.5	8.37E+11	0.13	37.8	1.81E+05	1.48E+06	0.12
	300	55.43	84.5	8.37E+11	0.09	37.8	1.87E+05	1.48E+06	0.13
	50	37.85	74.0	4.17E+11	0.23	37.8	8.22E+04	1.48E+06	0.06
	100	37.85	74.0	4.17E+11	0.13	37.8	9.01E+04	1.48E+06	0.06
	150	37.85	74.0	4.17E+11	0.09	37.8	9.31E+04	1.48E+06	0.06
	200	37.85	74.0	4.17E+11	0.07	37.8	9.46E+04	1.48E+06	0.06
	300	37.85	74.0	4.17E+11	0.04	37.8	9.62E+04	1.48E+06	0.06
	50	20.28	74.0	1.20E+11	0.08	37.8	2.69E+04	1.48E+06	0.02
	100	20.28	74.0	1.20E+11	0.04	37.8	2.77E+04	1.48E+06	0.02
	150	20.28	74.0	1.20E+11	0.03	37.8	2.80E+04	1.48E+06	0.02
	200	20.28	74.0	1.20E+11	0.02	37.8	2.81E+04	1.48E+06	0.02
	300	20.28	74.0	1.20E+11	0.01	37.8	2.83E+04	1.48E+06	0.02
	50	55.43	74.0	8.95E+11	0.41	37.8	1.47E+05	1.48E+06	0.10
	100	55.43	74.0	8.95E+11	0.24	37.8	1.74E+05	1.48E+06	0.12
	150	55.43	74.0	8.95E+11	0.17	37.8	1.86E+05	1.48E+06	0.13
	200	55.43	74.0	8.95E+11	0.13	37.8	1.92E+05	1.48E+06	0.13
	300	55.43	74.0	8.95E+11	0.09	37.8	1.99E+05	1.48E+06	0.13
	100	37.85	95.0	3.68E+11	0.11	37.8	8.04E+04	1.48E+06	0.05
	150	37.85	95.0	3.68E+11	0.08	37.8	8.28E+04	1.48E+06	0.06
	200	37.85	95.0	3.68E+11	0.06	37.8	8.40E+04	1.48E+06	0.06
	100	20.28	95.0	1.06E+11	0.03	37.8	2.46E+04	1.48E+06	0.02
	150	20.28	95.0	1.06E+11	0.02	37.8	2.48E+04	1.48E+06	0.02
	200	20.28	95.0	1.06E+11	0.02	37.8	2.49E+04	1.48E+06	0.02
	100	55.43	95.0	7.90E+11	0.22	37.8	1.57E+05	1.48E+06	0.11
	150	55.43	95.0	7.90E+11	0.16	37.8	1.66E+05	1.48E+06	0.11
	200	55.43	95.0	7.90E+11	0.12	37.8	1.71E+05	1.48E+06	0.12
	100	37.85	96.2	3.66E+11	0.11	37.8	8.00E+04	1.48E+06	0.05
	150	37.85	96.2	3.66E+11	0.08	37.8	8.23E+04	1.48E+06	0.06
	200	37.85	96.2	3.66E+11	0.06	37.8	8.35E+04	1.48E+06	0.06
k_-:	150	37.85	84.5	3.90E+11	0.08	13.4	1.65E+09	2.79E+10	0.06
	150	37.85	96.2	3.66E+11	0.08	13.4	1.55E+09	2.79E+10	0.06

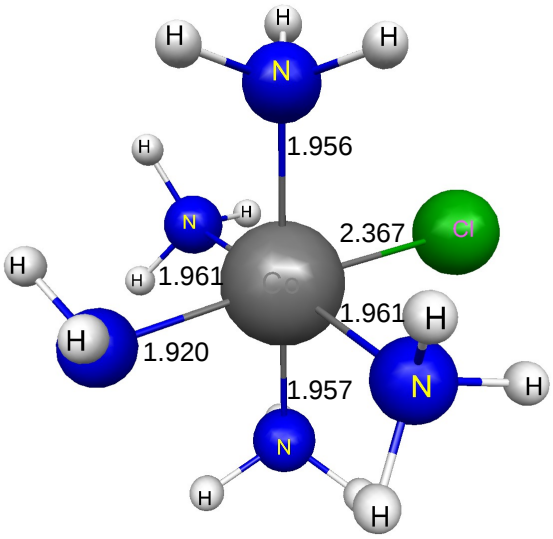

Figure S1. Perspective view and cobalt(III)−ligand bond lengths (Å) of the conjugate base *trans*-$Co(NH_3)_4(NH_2)Cl^+$ (angle between Co−N bond and NH_2^- plane: 115.9°).

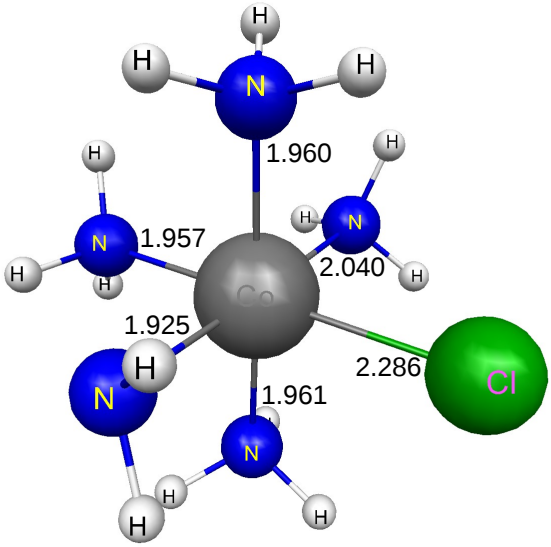

Figure S2. Perspective view and cobalt(III)−ligand bond lengths (Å) of the conjugate base *cis*-$Co(NH_3)_4(NH_2)Cl^+$ (angle between Co−N bond and NH_2^- plane: 113.8°).

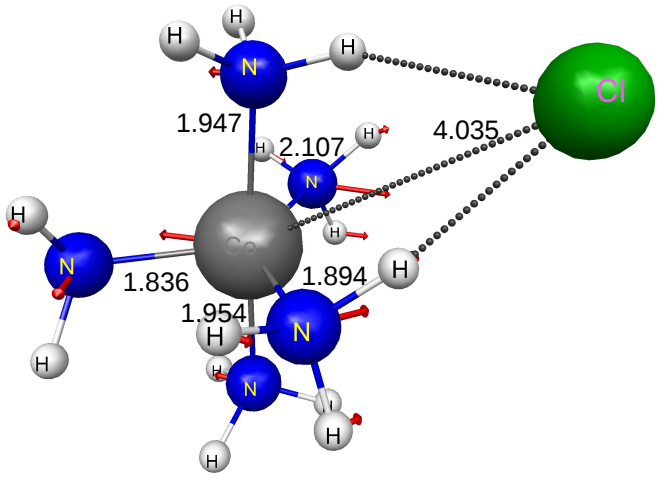

Figure S3. Perspective view, imaginary mode (163*i* cm^{-1}), and cobalt(III)−ligand bond lengths (Å) of the transition state *trans*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$.

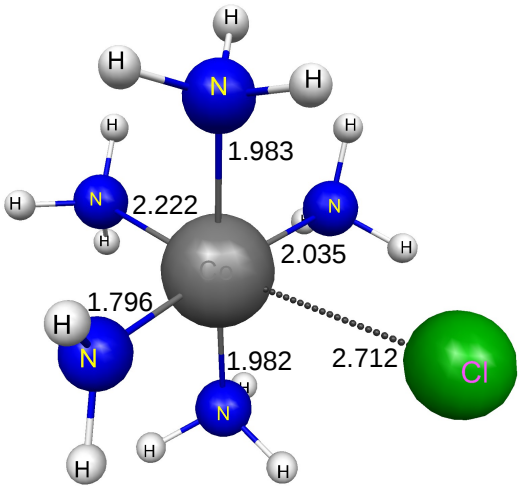

Figure S4. Perspective view and cobalt(III)−ligand bond lengths (Å) of the hexacoordinated intermediate *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^+$.

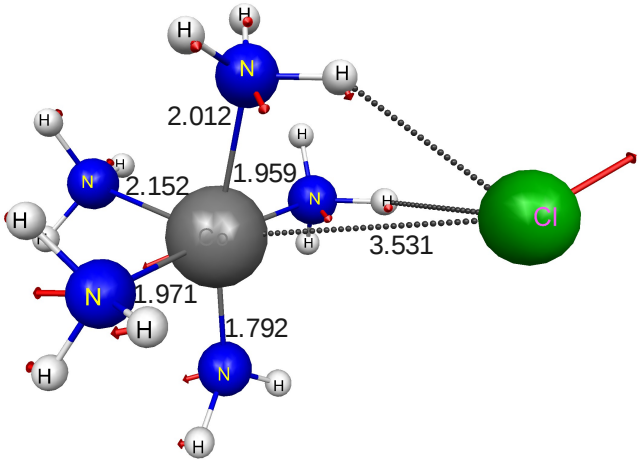

Figure S5. Perspective view, cobalt(III)−ligand bond lengths (Å), and imaginary mode (34*i* cm^{-1}) of the transition state *cis*-$Co(NH_3)_4(NH_2)\cdots Cl^{+\ddagger}$ (triplet state).

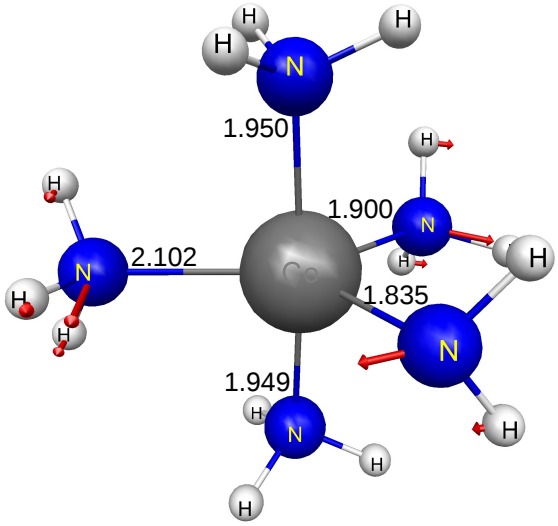

Figure S6. Perspective view, cobalt(III)−ligand bond lengths (Å), and imaginary mode (166*i* cm^{-1}) of the first transition state $Co(NH_3)_4(NH_2)^{2+\ ‡}$ for the Berry pseudo-rotation (singlet state). The angle between the 1.900 and 2.102 Å Co–N bonds of 139.8° is opened.

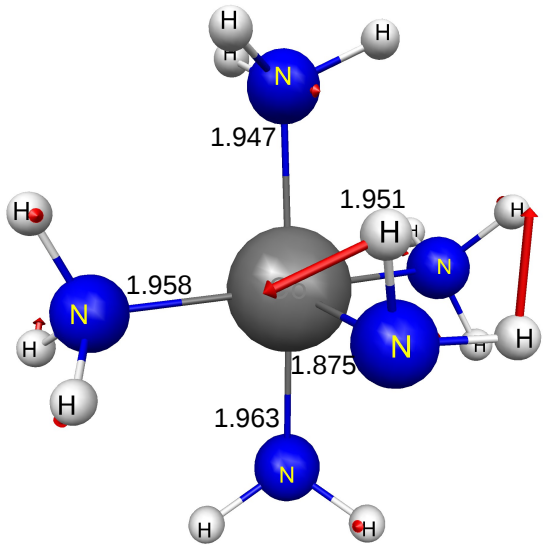

Figure S7. Perspective view, cobalt(III)−ligand bond lengths (Å), and imaginary mode (127*i* cm^{-1}) of the second transition state *ap*-*sqp*-$Co(NH_3)_4(NH_2)^{2+}$ ‡ for the Berry pseudo-rotation (singlet state).

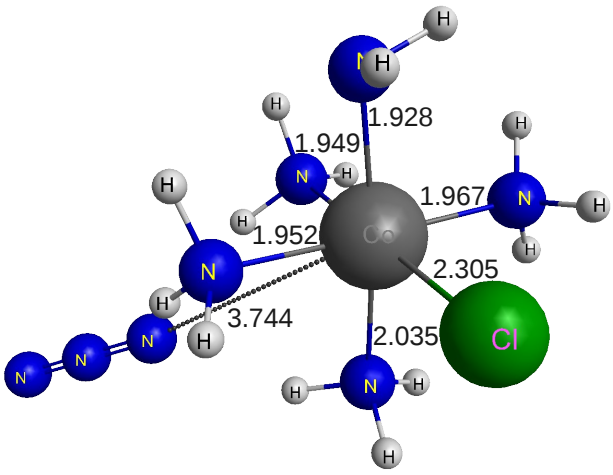

Figure S8. Perspective view and cobalt(III)−ligand bond lengths (Å) of the reactant *cis*-$Co(NH_3)_4(NH_2)Cl{\cdot}N_3$ (singlet state).

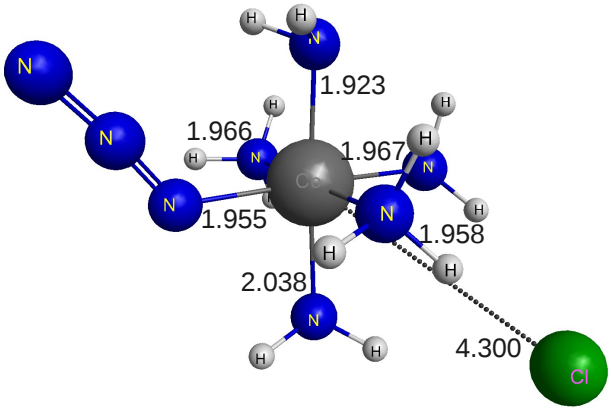

Figure S9. Perspective view and cobalt(III)−ligand bond lengths (Å) of the product *cis*-$Co(NH_3)_4(NH_2)(N_3)\cdot Cl$ (singlet state).

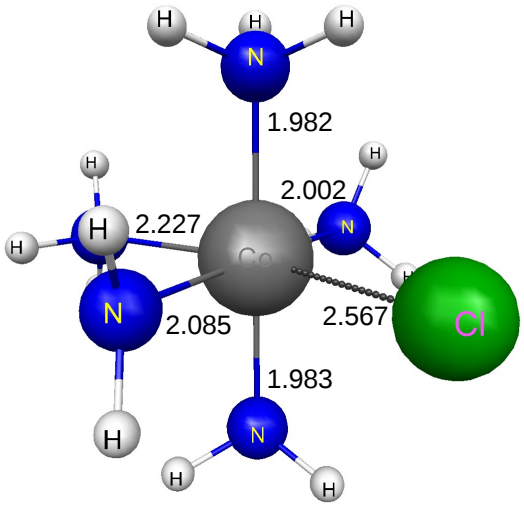

Figure S10. Perspective view and cobalt(II)−ligand bond lengths (Å) of the charge transfer intermediate *cis*-$Co^{II}(NH_3)_4(NH_2^{\bullet})\cdots Cl^{+}$.

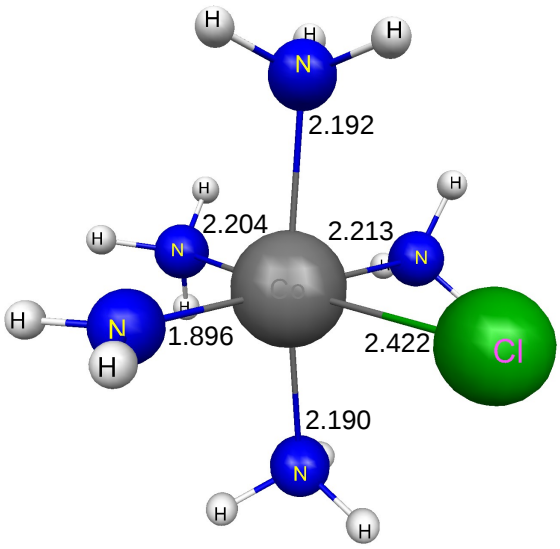

Figure S11. Perspective view and cobalt(III)−ligand bond lengths (Å) of the intermediate *cis*-$Co(NH_3)_4(NH_2)Cl^+$ in the quintet state.

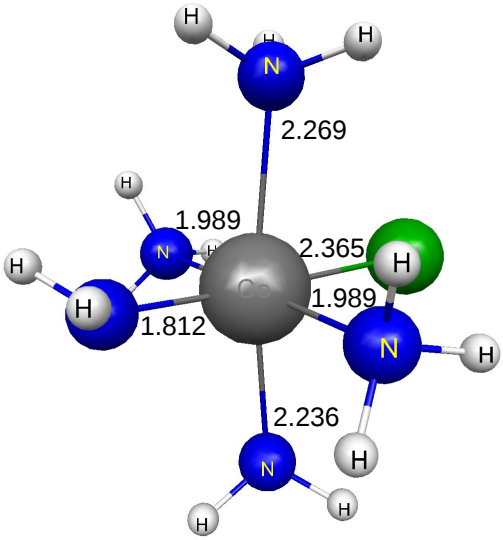

Figure S12. Perspective view and cobalt(III)−ligand bond lengths (Å) of the intermediate *trans*-$Co(NH_3)_4(NH_2)Cl^+$ in the triplet state.

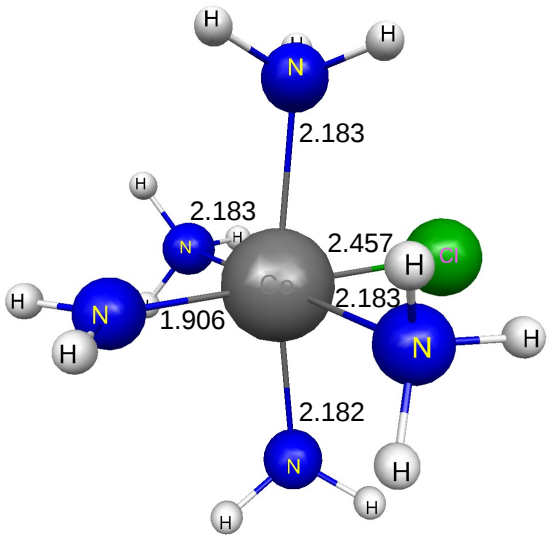

Figure S13. Perspective view and cobalt(III)−ligand bond lengths (Å) of the intermediate *trans*-$Co(NH_3)_4(NH_2)Cl^+$ in the quintet state.

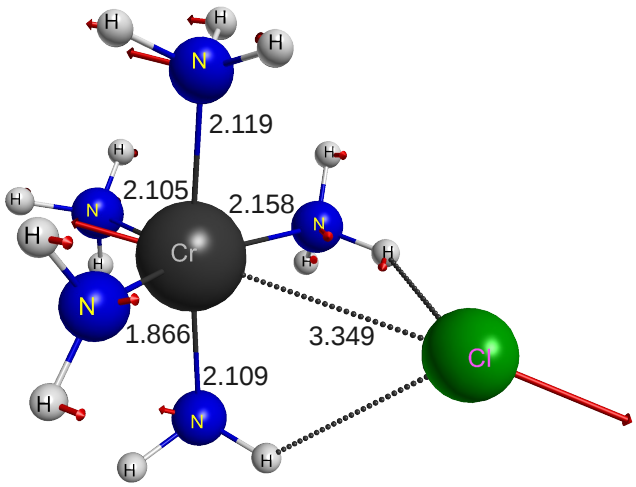

Figure S14. Perspective view, chromium(III)−ligand bond lengths (Å), and imaginary mode (77*i* cm^{-1}) of the transition state *cis*-$Cr(NH_3)_4(NH_2)\cdots Cl^{+\ \ddagger}$ (for the by Basolo-Pearson[17] mechanism).